

Quantification of Oxygenated Polycyclic Aromatic Hydrocarbons in the Vicinity of the Former Gasworks at Bay Shore, New York

Shawn Fisher¹

Paul Misut¹, Ronald Paulsen², and Stephen Zaugg³

¹ United States Geological Survey, Coram, NY

² Suffolk County Department of Health Services

³ USGS National Water Quality Lab, Denver, CO



Presentation Outline

Describe contamination area and remediation processes to date

Outline oxygenated PAHs and PAHs in modified lab methods

Show results of oxy-PAH sampling

Discuss the potential implications and need for continued monitoring

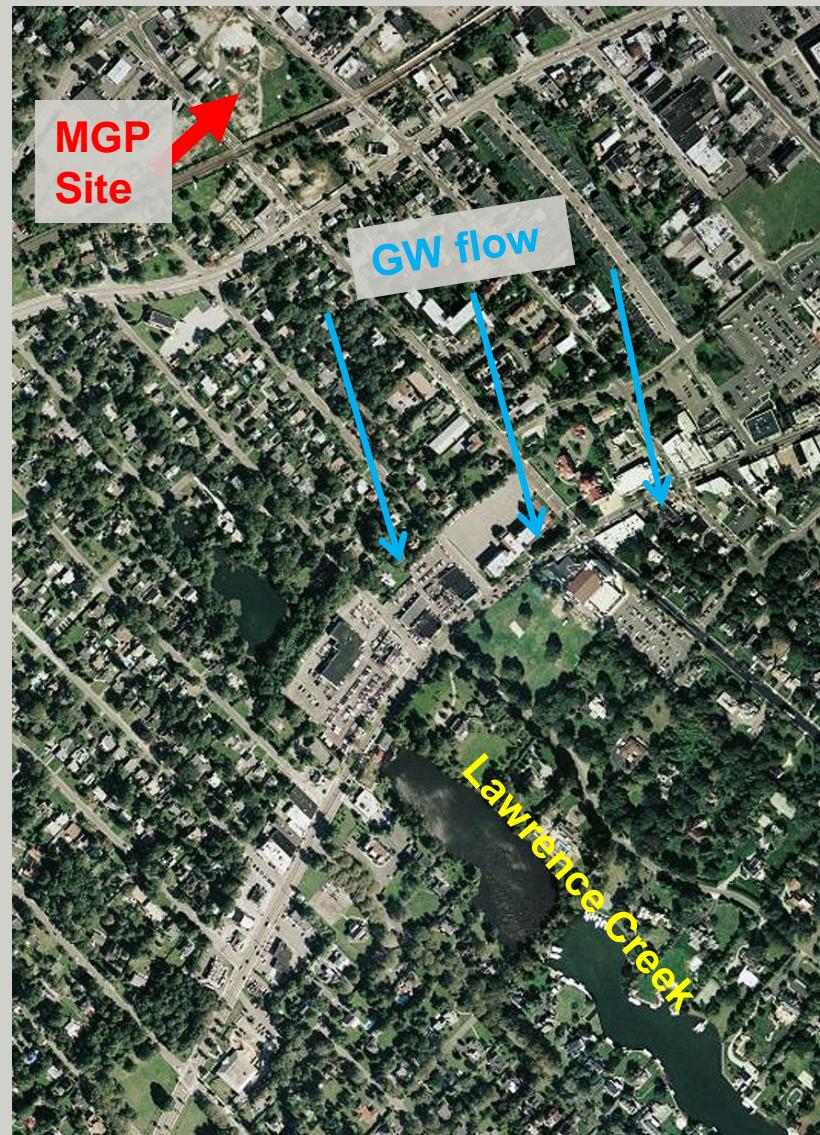
Bay Shore, NY

South shore of Long Island

Glacial material: sand
underlain by clay at 80 ft. BLS

Groundwater flow: Horizontal
movement under ~ 120 private
properties @ about 1 ft./day

Groundwater-fed stream also
affected (Lawrence Creek);
feeds into Great South Bay



History

Operated 1889 to 1973

NY issues “area of concern” (AOC) designation in 1999; site becomes part of state voluntary MGP cleanup program, not listed as superfund site

Contaminant plume affects the Upper Glacial Aquifer extending down more than 40 feet in some areas



Remediation

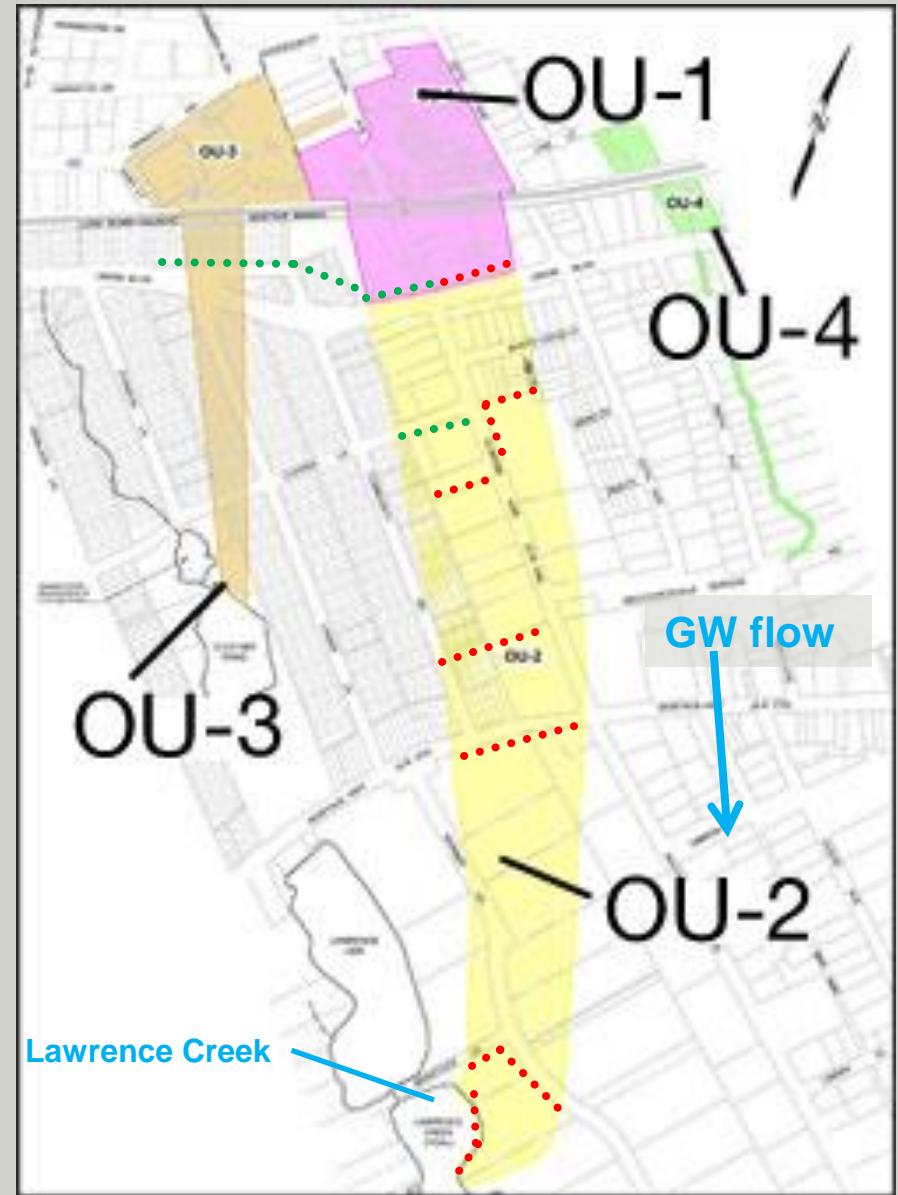
Operable Units (OU) depict plume boundaries

OU1: 100,000 tons of soil removed to date, pilot site for multiple In-Situ Chemical Oxidation (ISCO) tests beneath excavated areas

OU2: Oxygen-gas Injection (OGI) lines in service since 2005 in the lower portions of the plume, near Lawrence Creek. Additional oxygen injection lines completed 2008-2009

OU3: Original OGI site

OU4: Surfactant-ISCO comprehensive study; no OGI to date



..... 2005-2007 OGI

..... Recently activated OGI

Oxygenated Polycyclic Aromatic Hydrocarbons (oxy-PAHs)

Can be emitted from the same sources as PAHs

May be formed through both chemical (e.g. Fenton reagents) and biological (e.g. microbial) oxidation of PAHs in the environment

Oxidation enhances mobility due to increased polarity

Lundstedt et.al. compiled a list of oxy-PAHs and their toxicological effects on certain organisms that show some are more toxic than the parent PAH¹

Oxy-PAHs and former Gasworks

Study of the soils from Husarviken gasworks (Sweden)^{1,2} has shown that oxy-PAHs form and may accumulate as a result of the following oxidative treatments:

Pilot-scale bioslurry reactor

Lab-scale Fenton/Ethanol treatment

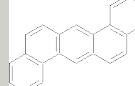
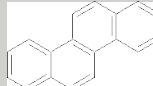
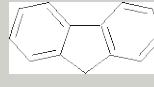
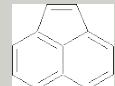
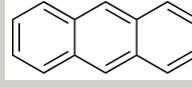
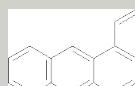
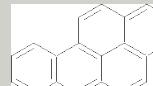
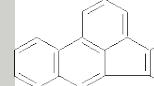
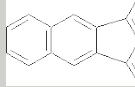
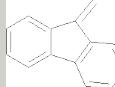
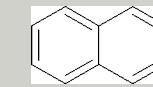
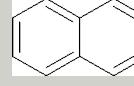
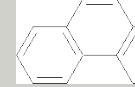
Mutagenic studies of *Salmonella* strains show oxidation products (including but not limited to oxy-PAHs) in bioslurry soils more toxic than PAH due to increased bioavailability²

In cooperation with the Suffolk County Department of Health Services, USGS has developed a method to monitor oxy-PAHs in groundwater at the Bay Shore former gasworks that may be associated with oxidative processes

oxy-PAHs analyzed

Compound	CAS number	Structure
9-Fluorenone	486-25-9	
Acenaphthenequinone	82-86-0	
9,10-Anthraquinone	84-65-1	
Phenathrene-1,4-dione	569-15-3	
4H-Cyclopenta[def]phenanthren-4-one	5737-13-3	
1,4-Anthraquinone	635-12-1	
9,10-Phenanthrenequinone	84-11-7	
Benzofluorenone	479-79-8	
Benzanthrone	82-05-3	
Aceanthracenequinone	6373-11-1	
7,12-Benz[a]anthracenquinone	2498-66-0	
Benzo[c]phenanthrene-[1,4]quinone	109699-80-1	
Benzo[cd]pyrenone	3074-00-8	
5,12-Naphthacenequinone	1090-13-7	

PAHs analyzed

Compound	CAS number	Detection Limit ($\mu\text{g/L}$)	Structure
Dibenz[a,h]anthracene	53-70-3	0.42	
Chrysene	218-01-9	0.32	
Fluorene	86-73-7	0.34	
Acenaphthene	83-32-9	0.28	
Acenaphthylene	208-96-8	0.3	
Anthracene	120-12-7	0.38	
Benz[a]anthracene	56-55-3	0.26	
Benzo[a]pyrene	50-32-8	0.32	
Benzo[b]fluoranthene	205-99-2	0.3	
Benzo[ghi]perylene	191-24-2	0.38	
Benzo[k]fluoranthene	207-08-9	0.3	
Fluoranthene	206-44-0	0.3	
Indeno[1,2,3-cd]pyrene	193-39-5	0.38	
Naphthalene	91-20-3	0.22	
Phenanthrene	85-01-8	0.32	
Pyrene	129-00-0	0.36	

Sample Preparation and Analysis

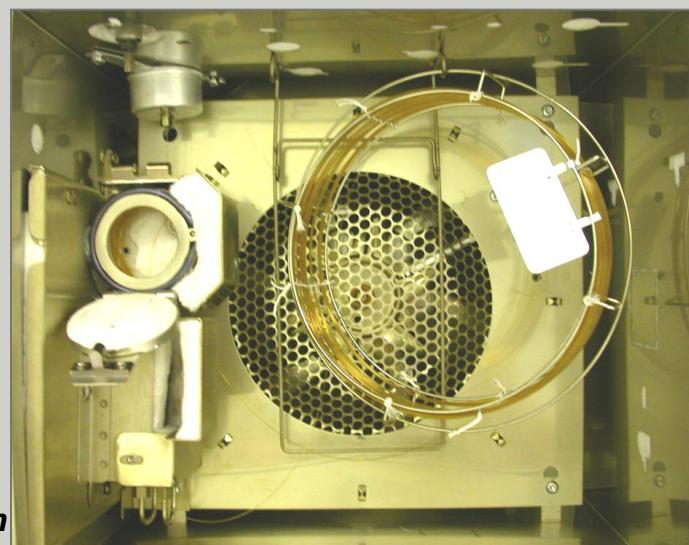
Sodium chloride added to sample and continuous liquid-liquid extraction is performed

Compounds separated using Gas Chromatography (GC) techniques

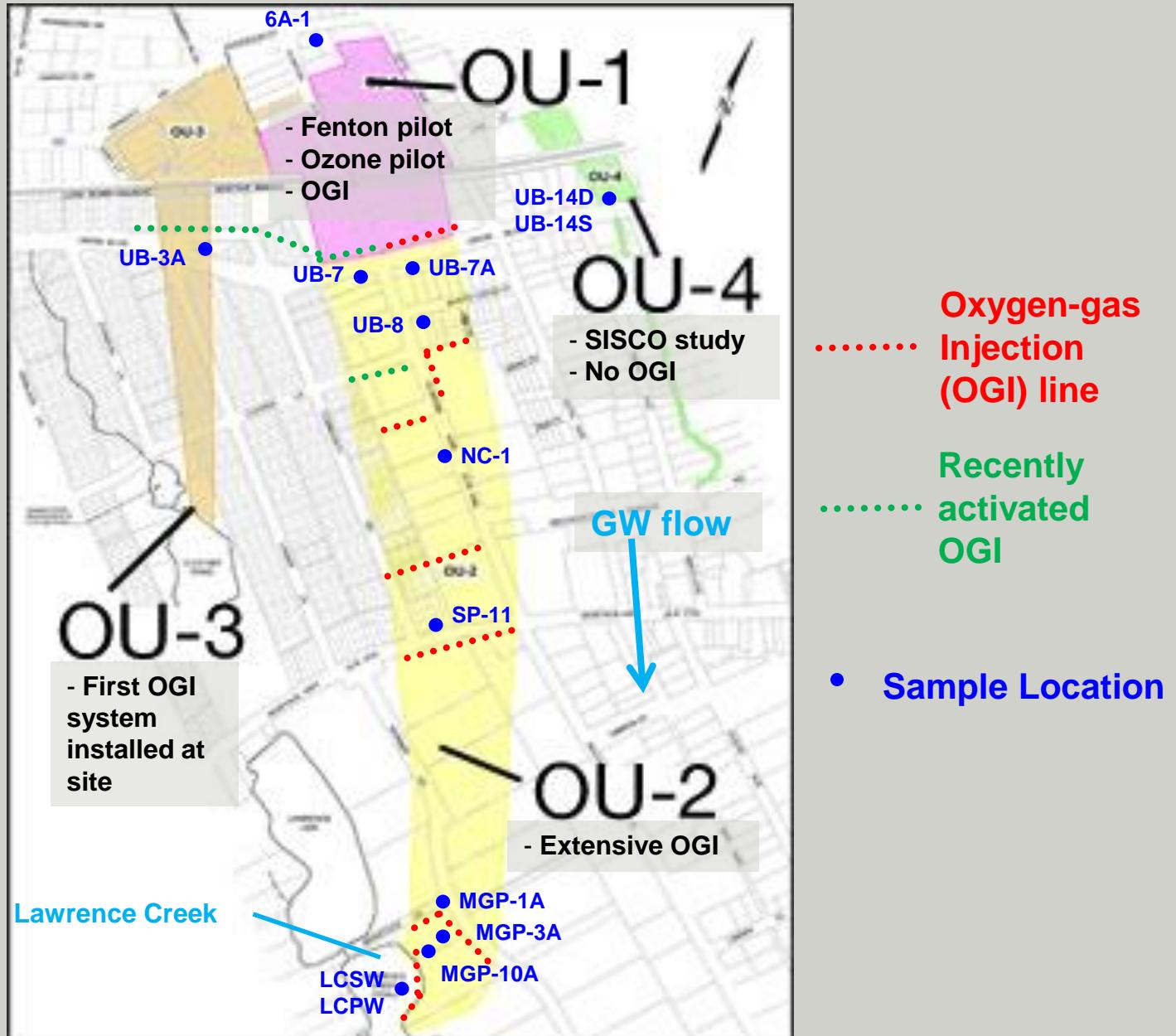
Characterized using Mass Spectrometry (MS) under Selected Ion Monitoring to obtain lower detection limits



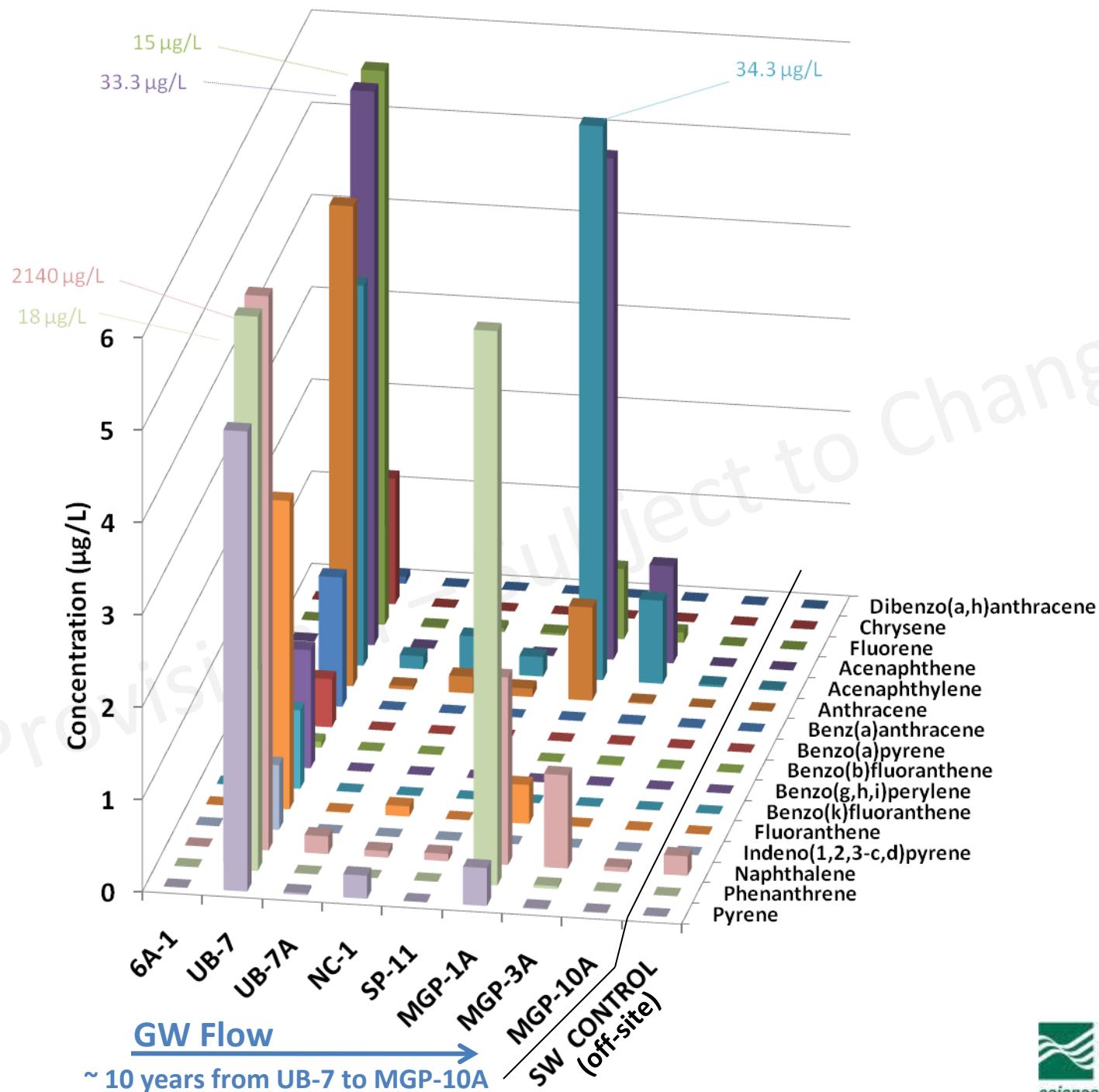
Gas Chromatograph – Mass Spectrometer



Sample Locations

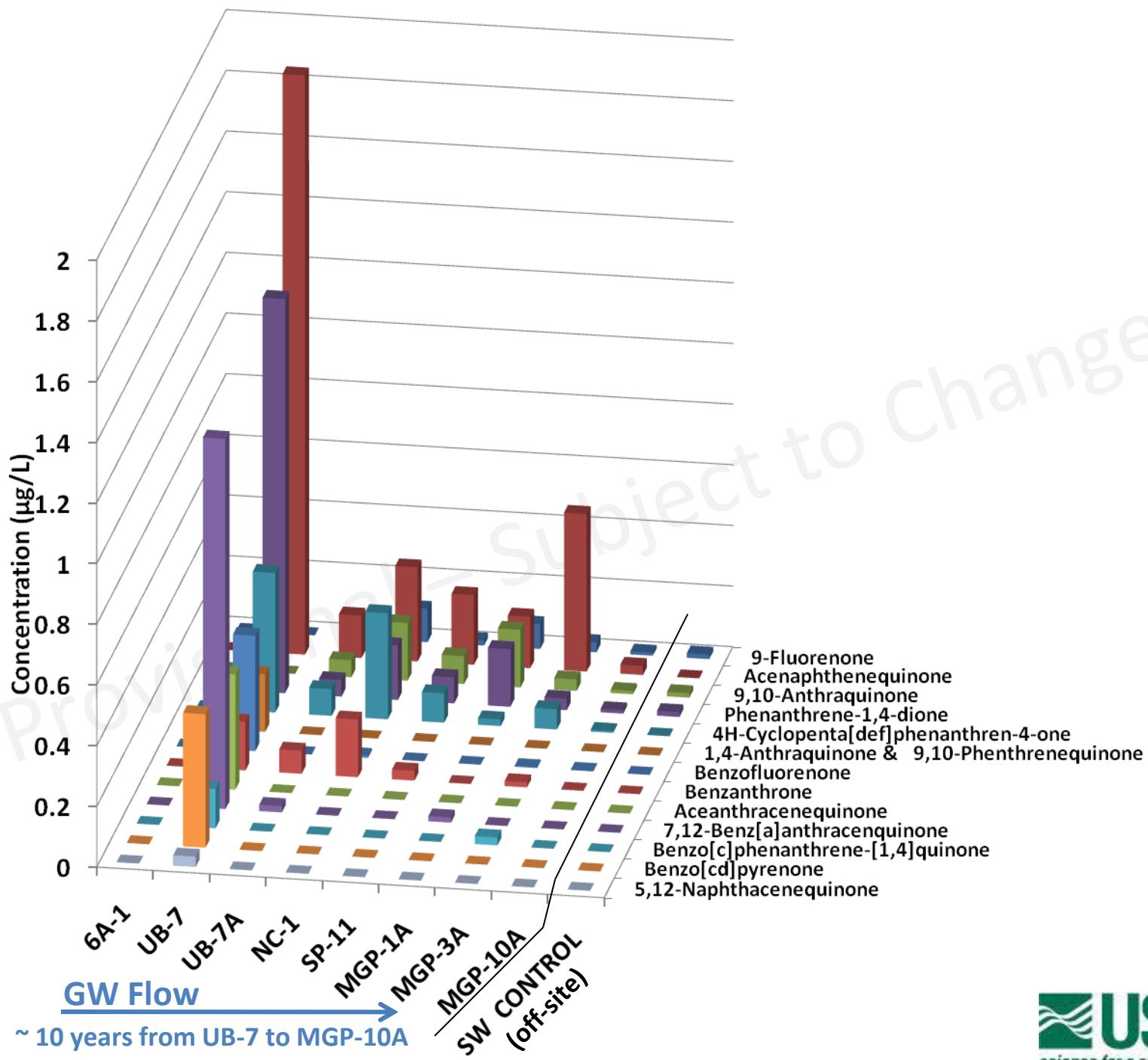


PAHs



6A-1,
up-gradient
CONTROL,
no detects

oxy-PAHs

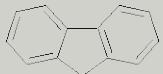


6A-1,
up-gradient
CONTROL,
no detects

PAH / oxy-PAHs Pairs

PAH

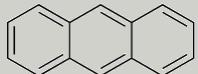
Fluorene



Acenaphthene & Acenaphthylene



Anthracene



Benz[a]anthracene



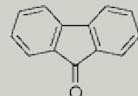
Phenanthrene



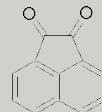
Biological or
Chemical
Oxidation

oxy-PAH

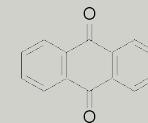
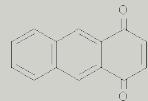
9-Fluorenone



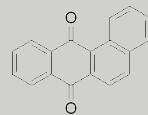
Acenaphthenequinone



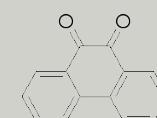
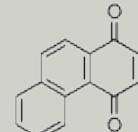
1,4-Anthraquinone & 9,10-Anthraquinone



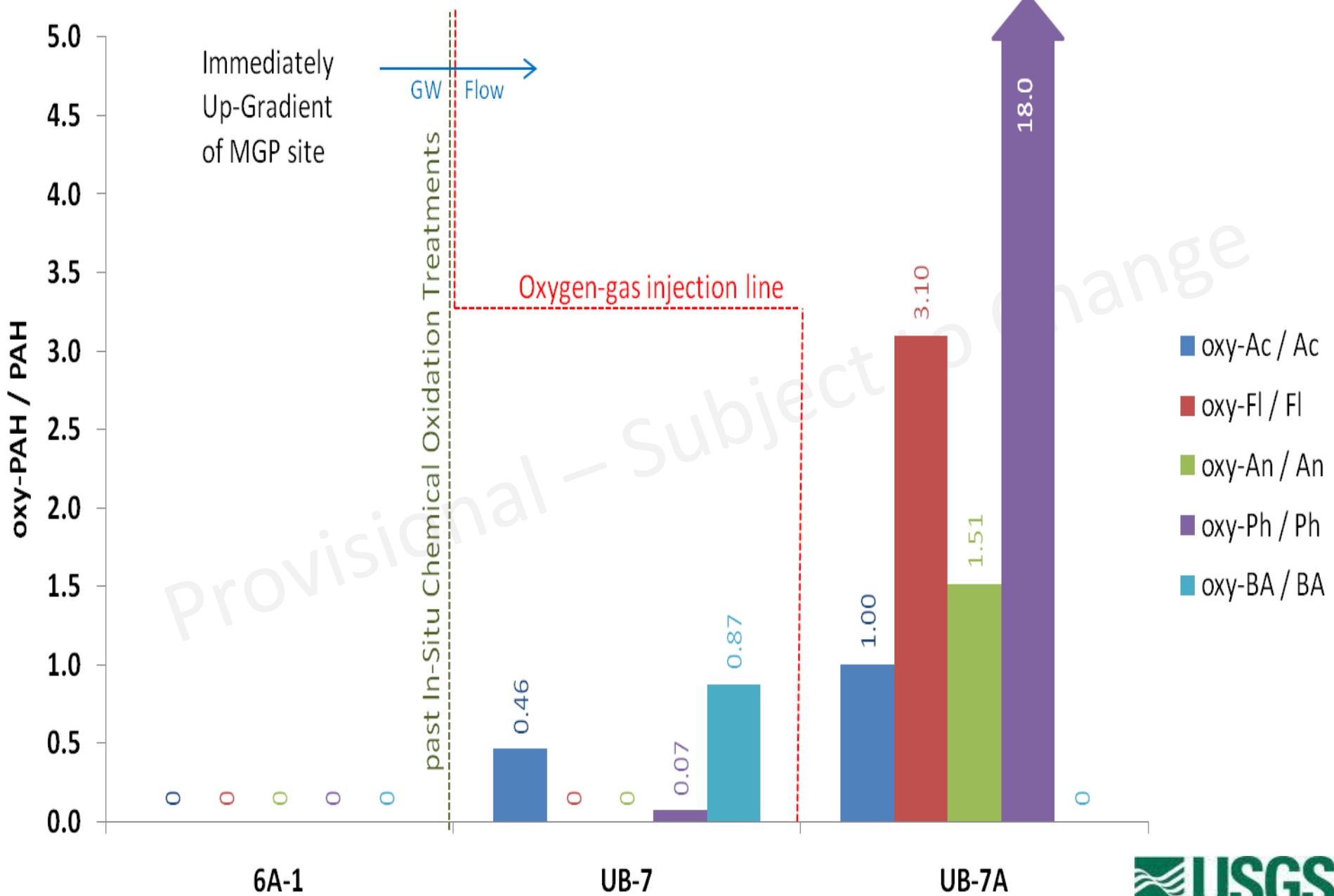
7,12-Benz[a]anthracenquinone



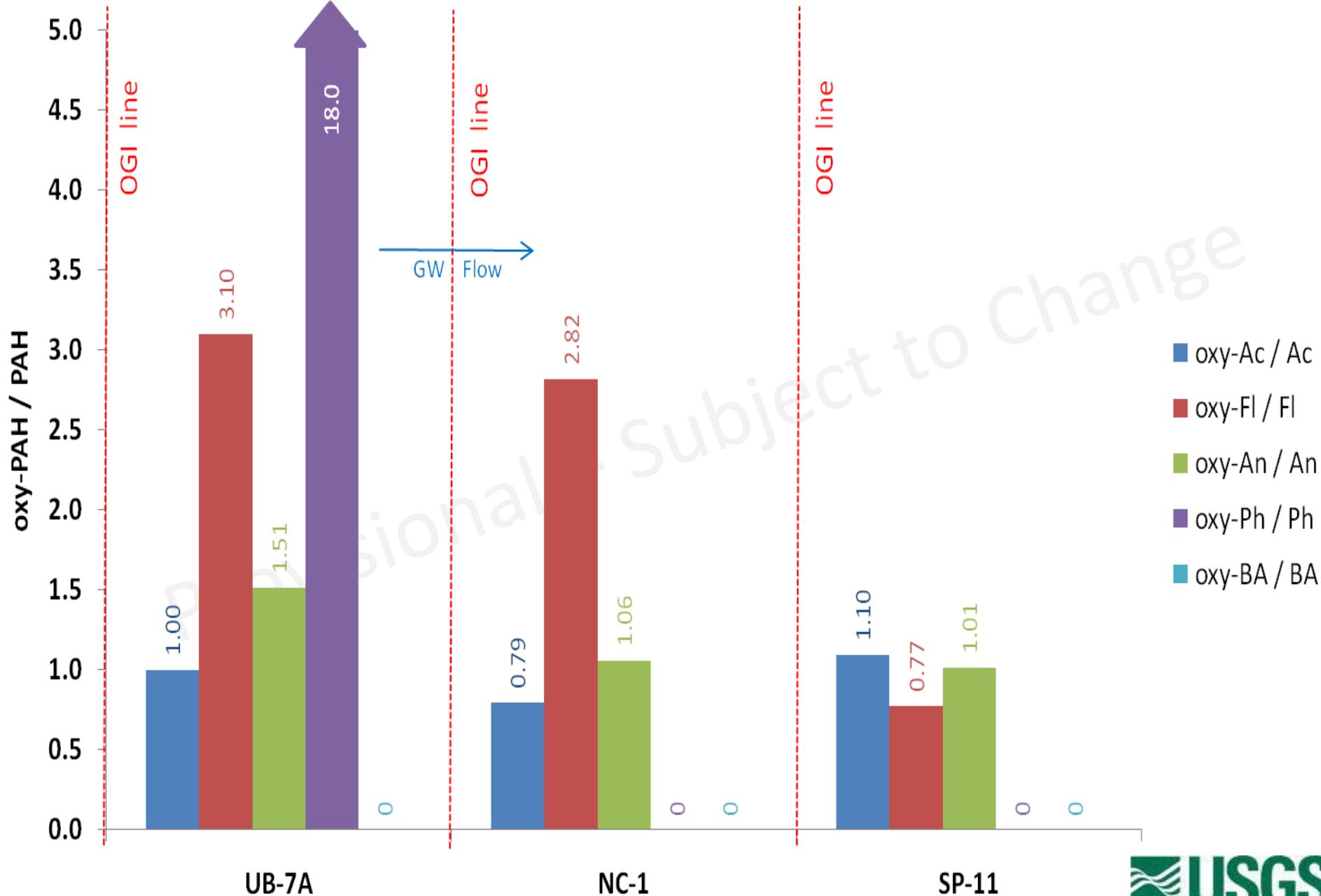
Phenathrene-1,4-dione & 9,10-Phenanthrenequinone



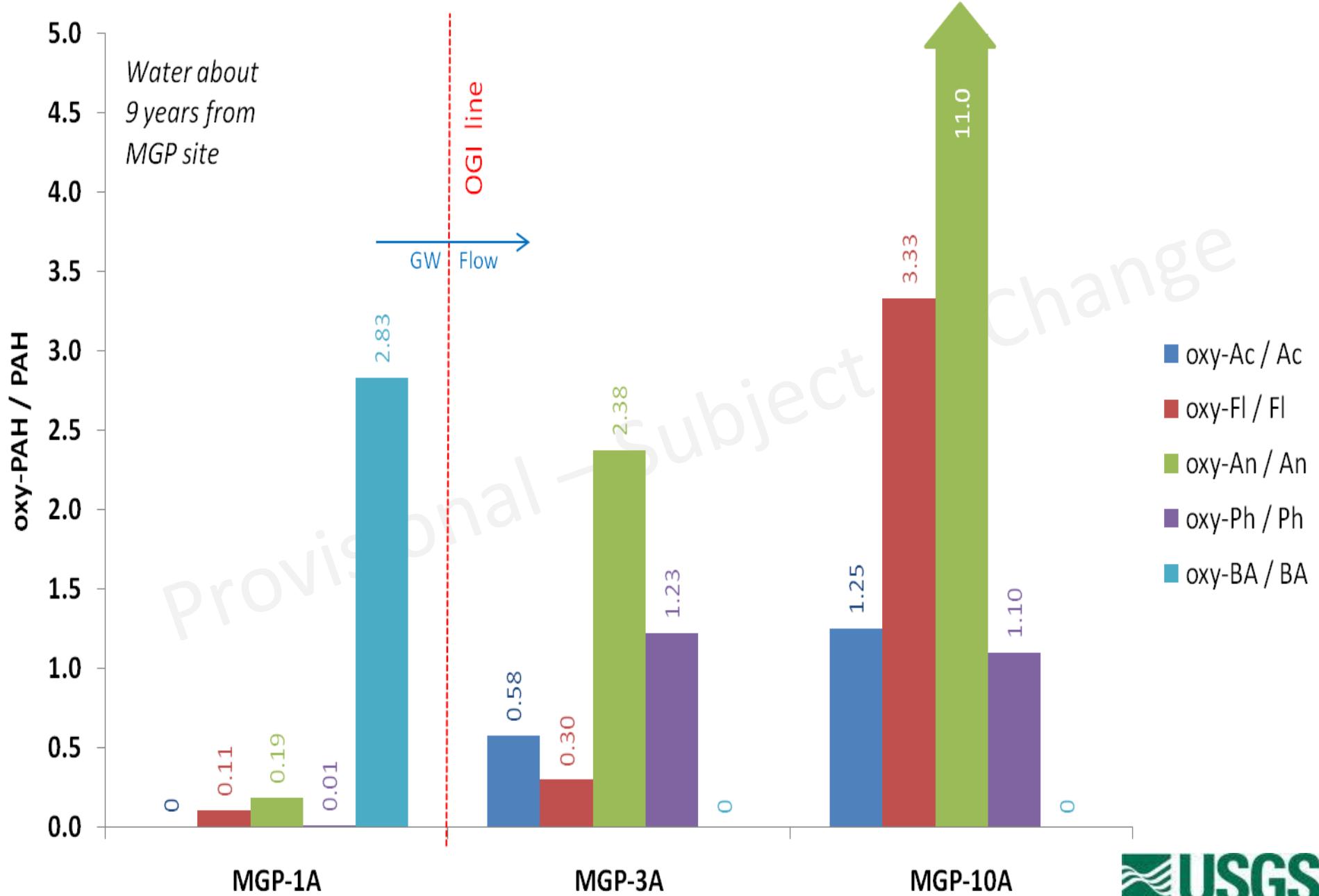
Ratio of oxy-PAH to their parent PAH



Ratio of oxy-PAH to their parent PAH



Ratio of oxy-PAH to their parent PAH



Conclusions

Significant amounts of PAHs and other organic compounds are present in some samples analyzed

Trace amounts of oxy-PAHs are present in most samples

Although concentrations are low, some oxy-PAH ratios compared to parent-PAHs are higher post-OGI system

This study demonstrated a method for the identification and quantification of some oxy-PAHs in ground water, though future work will likely expand this compound list based on the initial findings

Continuous (bi-annually) sampling is needed to monitor select wells and establish trends as remediation projects progress to lend more insight into the fate of PAHs in ground water undergoing oxidative treatment

References

Bay Shore site: <http://bayshoreworksmpg.com>

Toxicity:

http://proceedings.instep.ws/2006_04_02_MGP2006/content/pdf/04_Neuhauser_65.pdf

¹ Lundstedt S, White PA, Lemieux CL, Lynes KD, Lambert IB, et al. (2007) **Sources, Fate, and Toxic Hazards of Oxygenated Polycyclic Aromatic Hydrocarbons (PAHs) at PAH-contaminated Sites.** AMBIO: A Journal of the Human Environment: Vol. 36, No. 6 pp. 475–485

² Lemieux CL, Lynes KD, White PA, Lundstedt S, Oberg L, Lambert IB (2009) **Mutagenicity of an Aged Gasworks Soil During Bioslurry Treatment.** Environ Molec Mut, 50: 404-412

- OFR 93-125

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Method ID: O-3116-87

Thank-you

USGS

Water Resource Division

2045 Rt. 112

Coram. NY 11727

631 736 0783

scfisher@usgs.gov

pemisut@usgs.gov

*Suffolk County Department of Health
Services*

Office of Water Resources

360 Yaphank Ave
Yaphank, NY 11980

631 852 5801

ronald.paulsen@suffolkcountyny.gov

